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# SOVIET ARTICLE ON COLD-FLAME OXIDATION OF PROPANE

L. A. Repa and V. Ya. Shtern

The cold-flame oxidation of propage was investigated in the mixture Colls + O2. The experimental and analytical methods which we used have been described previously.[1] The exidation was carried out at T = 280° and Pinitial = 420 mm. Under these conditions, three cold-flame clashes arise during the course of the reaction.

The kinetics of the changes in pressure are shown graphically in Figure 1 [figures referred to are appended]. It is impossible to relate the peaks in the curve to the rapid increases and subsequent decreases in the number of particles in the mixture; it is much more probable that they originate from temperature changes. We therefore consider it permissible to plot a kinetic curve along those points which represent increases in pressure that are not connected with changes in temperature. When this is done, the usual S-shaped curve is obtained, the semilogarithmic anamorphosis of which yields a straight line (see Figure 2). As seen from curve w (Figure 5), the maximum velocity of the reaction, as computed from  $\Delta p$ , occurs at the moment when the first cold flame appears.

The kinetics of the accumulation of stable products of cold-flame chidation are shown by the data in Table 1 [appended]. These data indicate that a measurable reaction begins during the last part of the induction period. This behavior contrasts with that of propylene.[2] When propylene is oxidized, the quantities of aldehydes and peroxides reach their maximu at about the time the first cold flame appears, while in the case of propers, these products continue to accumulate up to the appearance of the third cold face. From this moment on, subsequent accumulation of aldehydes and peroxides ceases. When this happens, the amounts of HCHO and CH3CHO, present at the moment when the third

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cold flame originates, remain unchanged to the very end of the reaction, while the amount of peroxides sharply decreases during this last stage of oxidation. The accumulation of the other reaction products continues without any interruption throughout the course of the entire cold-flame oxidation. Note that the rate of increase in CO during each cold-flame period is significantly greater than that during the intervals between the flames.

It is interesting to note that, after a number of experiments have been run, a white, powdery coating forms on the cold connecting parts of the apparatus near the reaction vessel. This coating can be removed by careful heating with an alcohol burner and simultaneous evacuation with a pump.

Comperison of these results with those obtained in the investigation of the high-temperature oxidation of propane [1] leads to the conclusion that the chemistry of the oxidation of propane in both temperature ranges is very similar. In both cases, the total process of oxidation of propane consists of its actual oxidation and its cracking. For example, in the high-temperature oxidation of the mixture  $C_3H_8 + O_2$  at the end of the reaction taking place at  $350^\circ$ , the ratio of propane consumed in the oxidation to the propane cracked is 0.65.[3]

This ratio for the same mixture in the present work on the cold-flame reaction was found to be 0.66. A decrease in the ratio is perfectly natural, since a decrease in temperature (in changing over to cold-flame oxidation) has a greater effect on the cracking thun on the oxidation. The products (including the peroxides) of both phases [oxidation and cracking] of high-temperature and cold-flame oxidation are identical.

Furthermore, in the change from high-temperature to cold-flame oxidation of propane, there is no significant change in the quantitative relationship of reaction products. This is shown to be true by the data in Table 2 [appended], which correspond to the moment at the end of the reaction.

In investigating the high-temperature oxidation of propune ( $C_3 H_0 + O_2$ ,  $T = 350^\circ$ , Pinitial = 282 mm), it was found that the maximum velocity, as calculated from the increment in pressure, occurs at the moment when  $\Delta p = 17$  mm. Constant concentration of aldehydes and maximum concentration of peroxides are established at a later moment of the reaction, when  $\Delta p = 30$  mm. If there is really a congruence of chemical processes over the entire range of slow oxidation of hydrocarbons, then in the case of cold-flame oxidation of propose one can expect a similar congruence of the moment of maximum velocity, as calculated from the pressure increment, with the moment when the concentration of aldehydes becomes constant and the concentration of peroxides reaches a maximum.

Our data support this hypothesis. As we saw shove, the minimum velocity of cold-flame oxidation, as calculated from the pressure increment (after smitting the peaks), occurs at the moment when  $\Delta$  p = 15 mm; when  $\Delta$  p = 50 mm, the concentration of aldehydes becomes constant and the concentration of peroxides reaches a maximum (see Figure 3). This, undoubtedly, is an additional confirmation of the hypothesis that the same chemical processes comprise the basis for both high-temperature and cold-flame oxidation of propane.

From this point of view, cold-flame flashes merely represent insignificant side reactions and do not give rise to a measurable formation and accumulation of aldehydes and peroxides. Our results are in good agreement with this hypothesis of the nature of cold flames. In fact, as shown above,

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aldehydes and peroxides accumulate only during the occurrence of cold flames which are superimposed on the basic chemical process in that part of it where the maximum quantity of these products has not yet formed (first and second cold flames). However, if the cold flame originates after this moment, as for example the third cold flame does, it can no longer produce an additional accumulation of aldehydes and peroxides.

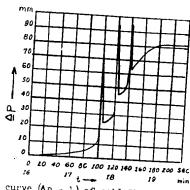


Figure 1. Kinetic curve (Ap - 1) of cold-flame exidation of the mixture  $C_3H_8 + O_2$ :

T = 280°; Pinitial = h20 mm

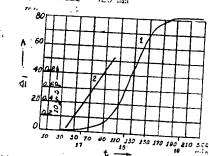


Figure 2. Kinetic curve of change of pressure in cold-fluxe exidation of prepane after emission of peaks (1) and its semilogarithmic argraphosis (2).

Mixture of C<sub>3</sub>H<sub>3</sub> + C<sub>2</sub>; T = 280°; Pinitial = 420 mm

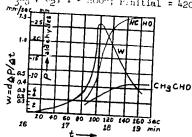


Figure 3. Rate of change of pressure (curve w) and of the concentrations of aldehydes (curves HCHO and CH<sub>3</sub>CHO) during course of cold-fluxe oxidation of mixture C<sub>3</sub>H<sub>8</sub> + O<sub>2</sub>; T = 280°; Pinitial = 420 mm

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Table 1. Analysis of the Mixture  $C_3H8 + O_2$  During the Course of Colu-Flame Oxidation T = 28%; Pinitial = 420 mm (case of three cold flames)

	Composition of Mixture (mm)										
Moment of Reaction	нсно	CHICHO	Percuide.	СИЗОН	Acido	_C. Ye	Calli.	<u> 11 _</u>	20	70.	<del></del>
17 min, 24 sec	4.3	2.9	1.3	9.2	3			-	- 20	<u> </u>	02
17 min, 39 sec	8.5	17	2.5	15.8	3.6						
Before 1st cold flame	12.5	9	2.:	17.7	4.6	. 1	3.5	3 0	13.0	6.U	183.0
End of " " "	16.1	5.	e :	25	3.8	14.0	5	F. 9	ب بان <u>ت</u> ن بانت		145.0
Before 2d " "	JU.9	6.0	3 7	30.0	5.3	1.5	6.7	5.1	31.5	11.6	-
End of " " "	23.2	7.0	1,	30.0	٤.5	17.5	6.0	é.4	54.5	13.4	125.0 92.0
Before 3a " "	-7.5	2.1	2.77	-1.0	5.4	1".9	11.5	6.2	60.5	19.6	67.6
End of " " "	47.9	7.05		h2.6	5.0	2	11.6	7 .	77.0	22.0	51.0
End of reaction	.K.5	2.5	2.35	45 ti	3.5	4.13	13.0	9.9	250,5	27.0	12.5

The peroxides consisted of approximately Per H2O2 and 30% organic peroxides, so it and ty polarographic and openical analysis.

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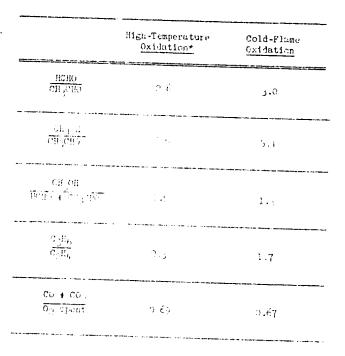
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Table 2. Reaction Product Ratios





\* Analytics, eat. Although in the axidation of the mixture delights, at T \*  $350^{\circ}$  and direction as the across of 1 for the absolution of the ration.[1]

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